

Simultaneous Removal of H₂S and NH₃ Using Metal Oxide Sorbents

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Introduction

Advanced coal gasification-based electric power plants such as integrated gasification combined cycle (IGCC) call for hot-gas cleanup following gasification in order to achieve high thermal efficiency. The Federal Energy Technology Center (FETC) hot-gas cleanup research program has focused on the development of high-temperature removal methods for particulates and chemical contaminants. Chemical contaminants that have received the most attention are sulfur gases, particularly hydrogen sulfide (H₂S). Development of metal oxide sorbents for high-temperature H₂S removal is a subject of intense research activity worldwide. However, other chemical contaminants such as nitrogen compounds must also be considered in the design of the hot-gas cleanup train.

During gasification, fuel-bound nitrogen in coal is principally released into the coal gas as ammonia (NH₃). When this coal gas is combusted in a gas turbine, NH₃ has the propensity to form oxides of nitrogen (NO_x) which are difficult to remove pollutants and precursors to “acid rain.” Thus, it is desirable to remove NH₃ from the coal gas before use in IGCC applications.

According to published data, the NH₃ concentration in coal gas can vary from 200 to 5,000 ppmv depending on the nitrogen content of coal and the configuration and operation of the gasifier. For example, the coal gas from a Texaco entrained-bed coal gasifier gasifying Illinois coal typically contains 1,800 to 2,000 ppmv NH₃. In contrast, a fixed-bed coal gasifier (e.g., Lurgi) typically produces about 5,000 ppmv NH₃, whereas a fluidized-bed coal gasifier (e.g., U-Gas, Kellogg) produces about 1,000 ppmv or less NH₃.

The NH₃ concentration in the exit coal gas appears to depend on the time-temperature history of the gas in the gasifier, with longer residence time at high temperature (~1,000 °C or higher) favoring removal of NH₃ by thermal decomposition [NH₃ → (1/2) N₂ + (3/2) H₂]. However, the NH₃ concentration does not reduce further via thermal decomposition once the fuel gas exits the gasifier because of the low temperature and short residence time in downstream process piping.

One potential approach for enhancing NH₃ decomposition would be to use a heterogenous catalyst in the hot-gas cleanup train to increase the decomposition rate. To be effective, the

catalyst must be active in the harsh coal gas environment and resistant to poisoning by H_2S , steam, and other gases.

SRI International identified Ni- and MoS_2 -based catalysts capable of decomposing NH_3 in hot coal-derived gas streams (Krishnan et al., 1988). The SRI study showed that in the absence of H_2S decomposition of NH_3 can be carried out readily in the temperature range of 550 to 800 °C using Ni-based catalysts. The SRI study demonstrated that HTSR-1, a proprietary Ni-based catalyst on a refractory support from Haldor-Topsoe, exhibited excellent activity and high-temperature stability. However, its tolerance to H_2S was found to be a function of temperature. Above 800 °C, no catalyst deactivation was observed even in gas streams containing 2,000 ppmv of H_2S . At lower temperatures, HTSR-1 deactivated rapidly when significant levels of H_2S were present in the fuel gas. Molybdenum-based catalysts were also investigated as potential NH_3 decomposition catalysts. Both General Electric (Ayala, 1993) and SRI International (Krishnan et al., 1988) have reported on the catalytic role of molybdenum sulfide (MoS_2) in ammonia decomposition.

Objectives

The objective of this project is to develop and demonstrate catalytic approaches for removing up to 90 percent of the NH_3 present in fuel gas at high-temperature, high-pressure (HTHP) conditions.

Approach

There are three potential methods of controlling NO_x emissions in IGCC systems. These include postcombustion selective catalytic reduction (SCR), turbine combustor modification, and NH_3 removal from HTHP fuel gas. SCR is proven technology for pulverized coal boilers but would be expensive for IGCC because of the requirement to treat a very dilute (typically containing less than 100 ppmv NO_x), large volume, low pressure turbine exhaust gas. While work is ongoing on the turbine combustor modification approach, it will be difficult to achieve a very high level of NO_x reduction in large-scale applications because of difficulties in scaleup. The method selected in this project was to develop catalysts for decomposing NH_3 in HTHP fuel gas. Since the gas is already available at HTHP conditions and it is relatively concentrated in NH_3 , this method is attractive. Research has been conducted on two potential approaches for removing NH_3 from HTHP fuel gas:

- High-temperature (800 to 900 °C) catalytic decomposition upstream of particulate and sulfur removal
- Simultaneous H_2S and NH_3 removal at 550 to 725 °C using metal oxide sorbent-catalysts.

Cobalt (Co), nickel (Ni), molybdenum (Mo) and tungsten (W) were evaluated as potential catalytic species. Results for the high-temperature catalytic decomposition approach were described in detail previously (Gangwal et al., 1996). The effort this year has concentrated on the simultaneous H_2S and NH_3 removal approach.

Project Description

Summary of Previous Work

Work in previous years consisted of thermodynamic evaluation, catalyst development for the high-temperature catalytic decomposition approach, and sorbent development for the simultaneous H₂S and NH₃ removal approach.

Thermodynamic Evaluation

Thermodynamic evaluations to determine the concentration of NH₃ in equilibrium with a Texaco gasifier gas showed that the extent of NH₃ decomposition is thermodynamically limited, but NH₃ decomposition >90 percent is possible in the temperature range of 500 to 900 °C. In the 500 to 600 °C range, methane (CH₄) formation is favored. This reduces the H₂ and promotes the NH₃ decomposition reaction $[\text{NH}_3 \rightarrow (\frac{1}{2}) \text{N}_2 + (\frac{3}{2}) \text{H}_2]$. As temperature is increased from 600 °C to 900 °C, the endothermic NH₃ decomposition is favored. At pressures up to 20 atm, the equilibrium NH₃ level was calculated to be less than 160 ppmv in the 500 to 900 °C temperature range.

Thermodynamic evaluations were also performed to evaluate the stability of the catalytic species (Co, Ni, Mo, and W) in reducing, sulfiding, and oxidizing environments at HTHP conditions. All of the species (i.e., metals, sulfides, and oxides) were found to be stable under the conditions of interest. The only species with volatility of some concern was found to be molybdenum oxide. However, formation of bimetallics with other catalytic species was shown to reduce the volatility of molybdenum oxide by up to four orders of magnitude.

High-Temperature Catalytic Decomposition

A number of commercial catalysts were tested for this approach. Based on these screening tests, HTSR-1 (a proprietary nickel-based catalyst from Haldor-Topsoe) was selected for long-term testing. Two 100-h tests were conducted using HTSR-1. The first 100-h test was conducted using a slipstream of actual coal gas from the U.S. Department of Energy (DOE)/Morgantown 10-in. fluidized-bed coal gasifier. A 3.0-in. diameter reactor housed inside RTI's mobile laboratory was used for this test that was conducted at 146 psig (10.8 atm), 780 °C, and 4,975 std cm³/cm³·h space velocity. The NH₃ and H₂S concentrations in the inlet coal gas were 3,300 and 1,300 ppmv, respectively. The NH₃ decomposition averaged around 90 percent during the test and no catalyst deactivation occurred over the 100-h due to trace contaminants in coal gas.

The second 100-h test was conducted by General Electric using simulated Texaco coal gasifier gas with inlet NH₃ and H₂S concentrations of 7,500 and 1,550 ppmv, respectively. The reactor used had an internal diameter of 2.15 cm and the conditions used were 8.5 atm, 900 °C, and 5,000 to 10,000 std cm³/cm³·h. During the first 40 h, some catalyst deactivation was seen, but the activity stabilized. The average NH₃ decompositions were 80 and 88 percent at 10,000 and 5,000 std cm³/cm³·h, respectively.

Simultaneous NH₃ and H₂S Removal

Several catalysts containing Ni, Co, Mo, and W (with Al₂O₃, TiO₂, and other oxides as supports) were prepared and tested by themselves or in combination with a zinc titanate sorbent at 725 °C. However, none of these materials exhibited significant NH₃ decomposition activity in simulated Texaco coal gas containing 7,500 ppmv H₂S. In a parallel project (DOE Contract No. DE-FG22-93MT93005) between Hampton University and RTI, the HART series of mixed-metal oxide sorbents was developed for simultaneous NH₃ and H₂S removal (Jothimurugesan and Gangwal, 1996). A promising HART-49 sorbent-catalyst recipe was identified for further development this year under the current project. The HART-49 sorbent-catalyst was a zinc-based material containing 5 wt% each of Ni, Co, and Mo (the preparation procedure is proprietary). The BET surface area of this material was 4.7 m²/g. In a 1-g fixed-bed microreactor, at 1 atm and 500–700 °C, this material showed decomposition of >90 percent NH₃ and removal of H₂S to <20 ppmv over a substantial portion of the desulfurization cycle. This paper concentrates on the results of the HART-49 sorbent powder and its derivatives in fluidizable, attrition-resistant form.

Experimental Apparatus/Conditions

The experiments this year were conducted in two scales and types of equipment: 1) a bench-scale 2.0-inch fluidized-bed HTHP reactor; and 2) a fixed-bed HTHP microreactor. The bench-scale fluidized-bed reactor system is shown in Figure 1. The fixed-bed microreactor was essentially similar to this system except for the scale of equipment and was described previously (Jothimurugesan and Gangwal, 1996). As seen in Figure 1, simulated coal gas was generated using a battery of mass flow controllers. The gas was preheated, mixed with steam, and passed into the reactor at desired flow. The H₂S in the outlet gas was measured using a gas chromatograph with a flame photometric detector. Continuous H₂S, SO₂, NO_x, and O₂ analyzers were also used as needed. The sorbent loads in the bench-scale reactor and microreactor systems were approximately 200 and 1 g, respectively. Simulated KRW gas was used in the tests. The gas composition and sulfidation reaction conditions are shown in Tables 1 and 2, respectively. The regeneration was conducted using 2 to 4 percent O₂ in N₂ at the same conditions as the sulfidation.

Ammonia in the outlet gas was captured using a water scrubber as shown in Figure 1. The water samples were collected and weighed periodically and the NH₃ was measured using either the ion chromatography or the ion selective electrode technique. The two methods had fair agreement with each other.

Results/Accomplishments

Results of the 10th, 20th, and 30th cycle of a 700 °C, 1 atm test with HART-49 powder are shown in Figure 2. As seen, the NH₃ removal was over 90 percent for the first 3 hours and then dropped to 40 percent. H₂S was removed to below 20 ppmv. The 3-h window for high NH₃

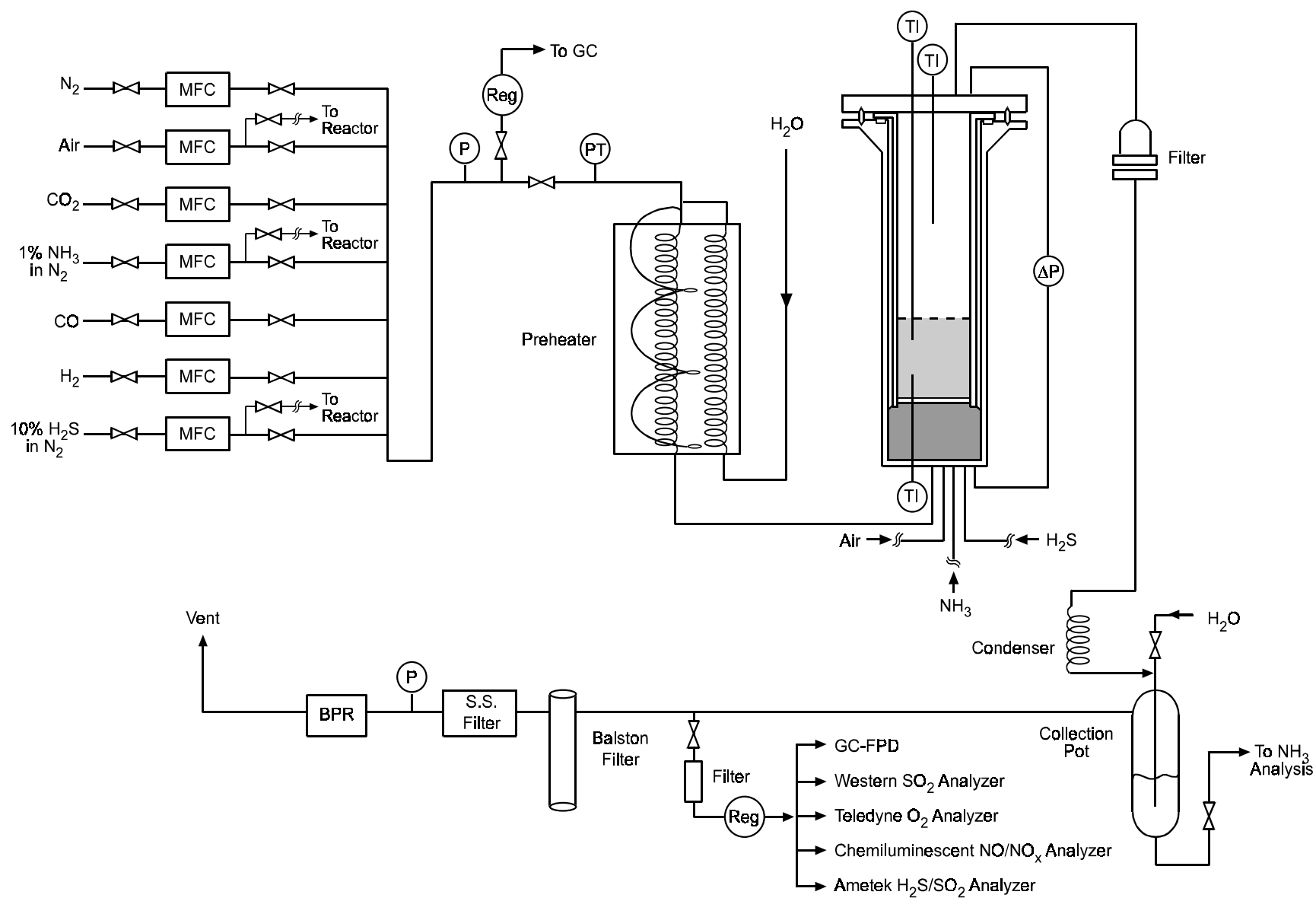


Figure 1. Bench-scale fluidized-bed reactor system.

Table 1. Simulated KRW Gas Composition

	Volume %
H ₂	11.0
CO	17.0
CO ₂	9.0
H ₂ O	5.0 to 15.0
H ₂ S	0.3 to 0.6
NH ₃	0.16 to 0.2
N ₂	Balance

Table 2. Reaction Conditions

	Bench-Scale Fluidized-Bed	Fixed-Bed Microreactor
Pressure (atm)	20	1 to 10
Temperature (°C)	550	550 to 700
Space Velocity $\left(\frac{sec}{cc \cdot h} \right)$	7,500	2,500

removals was quite encouraging. Furthermore, the dramatic effect of steam on NH₃ removal are seen in Figure 3. Note that NH₃ removal was essentially complete all the way until H₂S breakthrough in the absence of steam at 1 atm and 700 °C.

The testing emphasis this year shifted to lower temperatures and higher pressure. The effect of temperature reduction on the windows of high NH₃ removal by HART-49 powder is shown in Figure 4. Even at a temperature as low as 500 °C, NH₃ removal remained high for 70 min, up to about 6 wt% sulfur loading on the sorbent.

At this point, modifications were made to the HART-49 powder to develop it in attrition-resistant fluidizable form. The preparation is proprietary. After a number of trials, HART-55 sorbent was prepared. Its attrition resistance was better than commercial fluid catalytic cracking (FCC) catalysts used extensively in refineries. A high level of binder was incorporated in the sorbent to impart it a high degree of attrition resistance.

The effect of pressure on the window of high NH₃ removal by HART-55 is shown in Figure 5. As seen, pressure promotes the removal of NH₃. This is contradictory to thermodynamic predictions and indicates the possibility of NH₃ chemisorption on the sorbent, in addition to

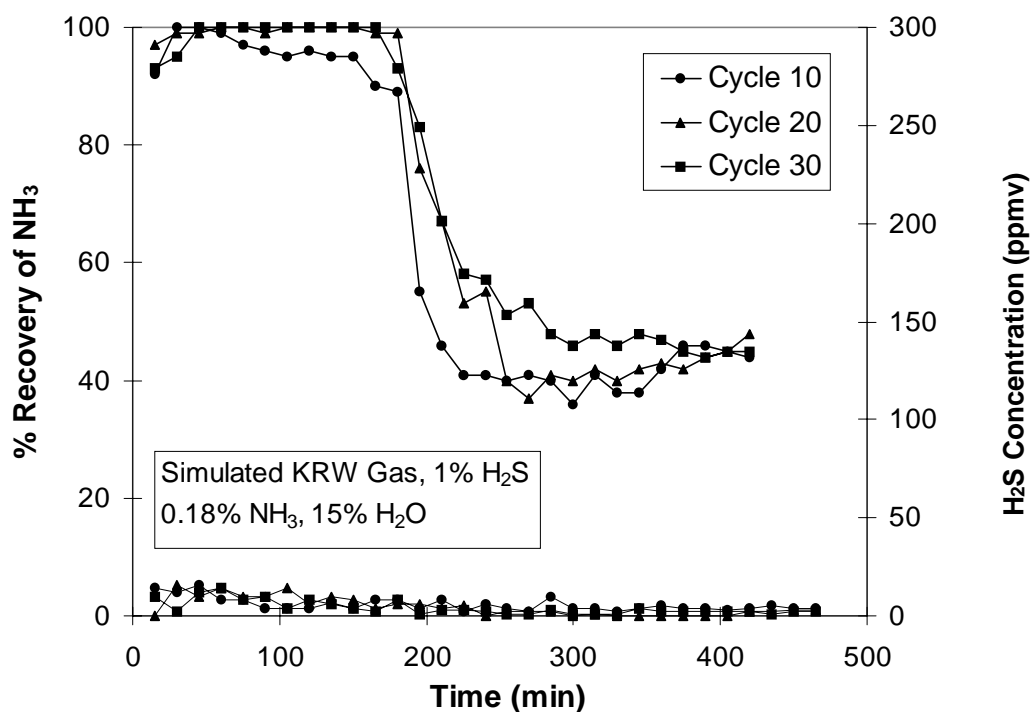


Figure 2. Simultaneous NH_3 and H_2S removal by HART-49 at 700°C and 1 atm.

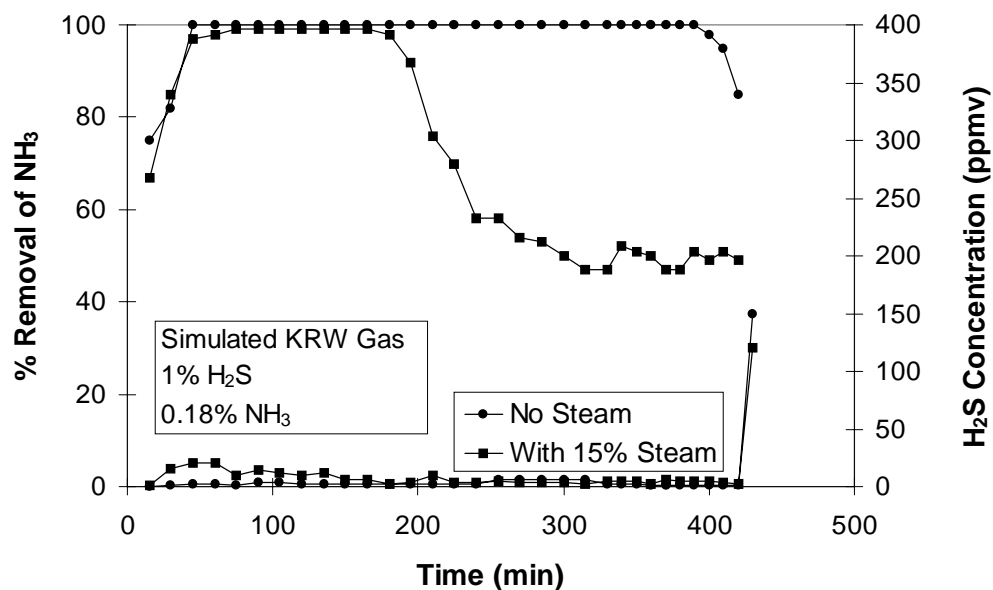


Figure 3. Effect of steam on NH_3 removal by HART-49 at 700°C and 1 atm.

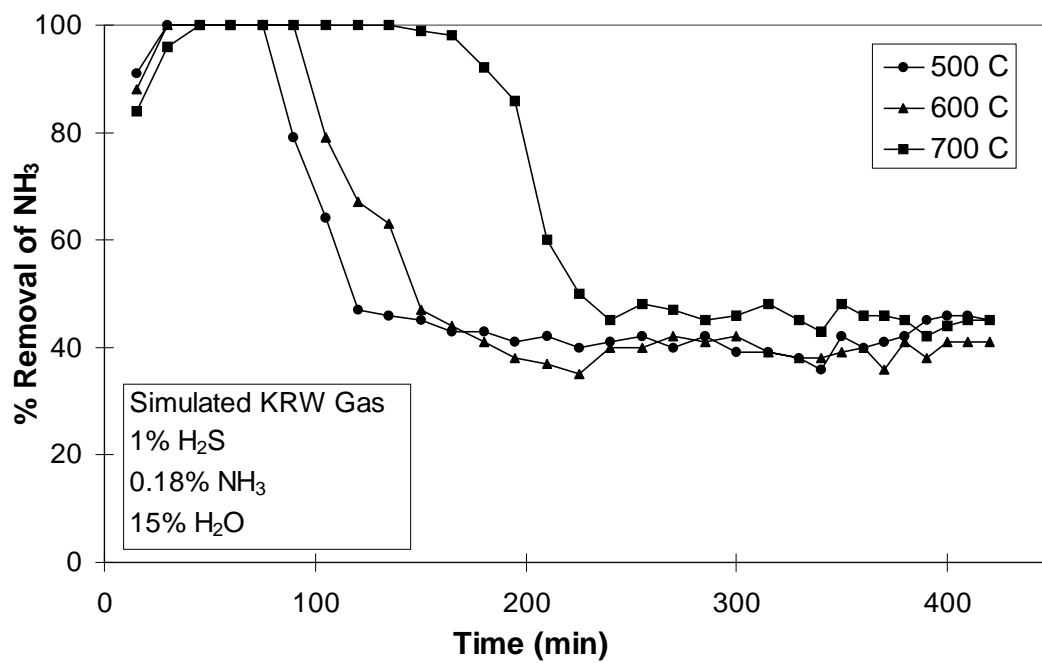


Figure 4. Effect of temperature on NH_3 removal by HART-49 at 1 atm.

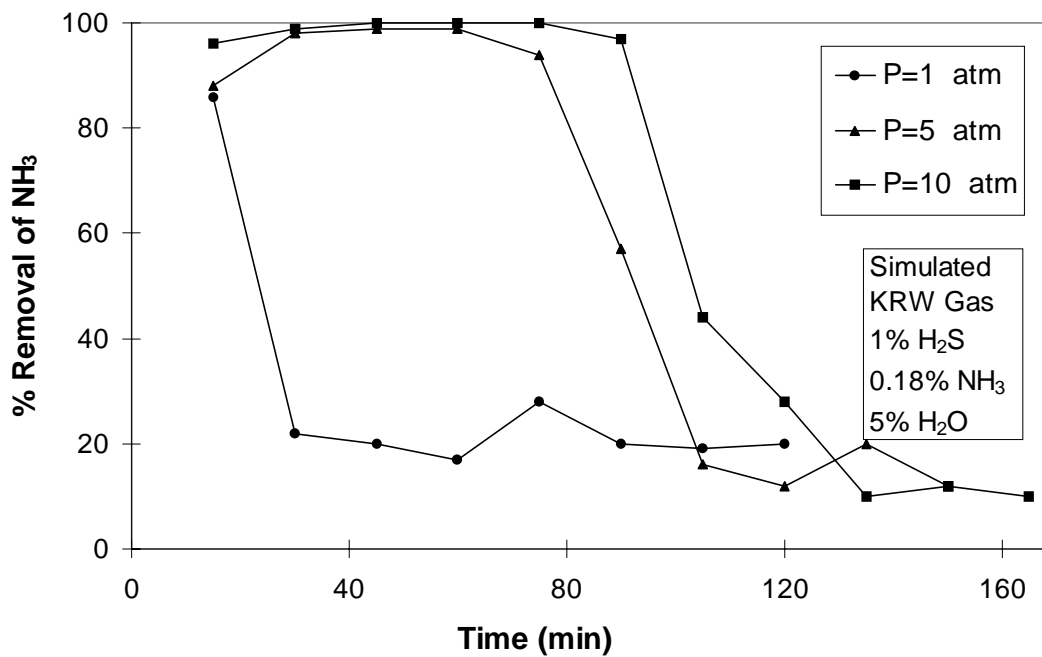


Figure 5. Effect of pressure on NH_3 removal by HART-55 at 550 °C.

decomposition. Some NH_3 release from the sorbent was observed during regeneration, which lends credence to the possibility of NH_3 chemisorption during sulfidation. Figure 6 shows the results of a seven-cycle test at 10 atm on HART-55. The consistent results over seven cycles show that the sorbent is behaving reproducibly after regeneration.

At this point the HART-55 sorbent-catalyst preparation was scaled up to prepare 200 g for the 20 atm fluidized-bed tests. The scaled-up material, designated HART-56, was tested over 20 cycles in the 2.0-in. bench-scale fluidized-bed reactor system. The average NH_3 and H_2S removal results for the first two cycles (with 5 percent steam in the KRW gas) are shown in Figure 7. A high degree of NH_3 and H_2S removal was achieved over the first two cycles, confirming the microreactor results of Figure 8. However, NH_3 was seen to elute from the material during purges and regeneration, again indicating chemisorption during sulfidation. Performance after the first two cycles, when steam in the coal gas was increased to 15 percent, deteriorated. The NH_3 balance over the 20 cycles is shown in Figure 8.

The reactor was purged with N_2 after both sulfidation (purge #1) and regeneration (purge #2) during the 20-cycle test. During regeneration, no NO or NO_2 was found in the regeneration tail gas. As seen, the average NH_3 accounted for during cycles 1 and 2 was about 59 percent, indicating only about 41 percent average removal during sulfidation. The average removal deteriorated significantly during cycles 3 to 20, carried out with 15 percent steam. The results indicate that HART-56 was not successful in achieving significant NH_3 removal at 550 °C and 20 atm except when 5 percent steam was present in the simulated coal gas. Also, reversible adsorption of NH_3 appeared to occur on the sorbent, which could be removed by purging.

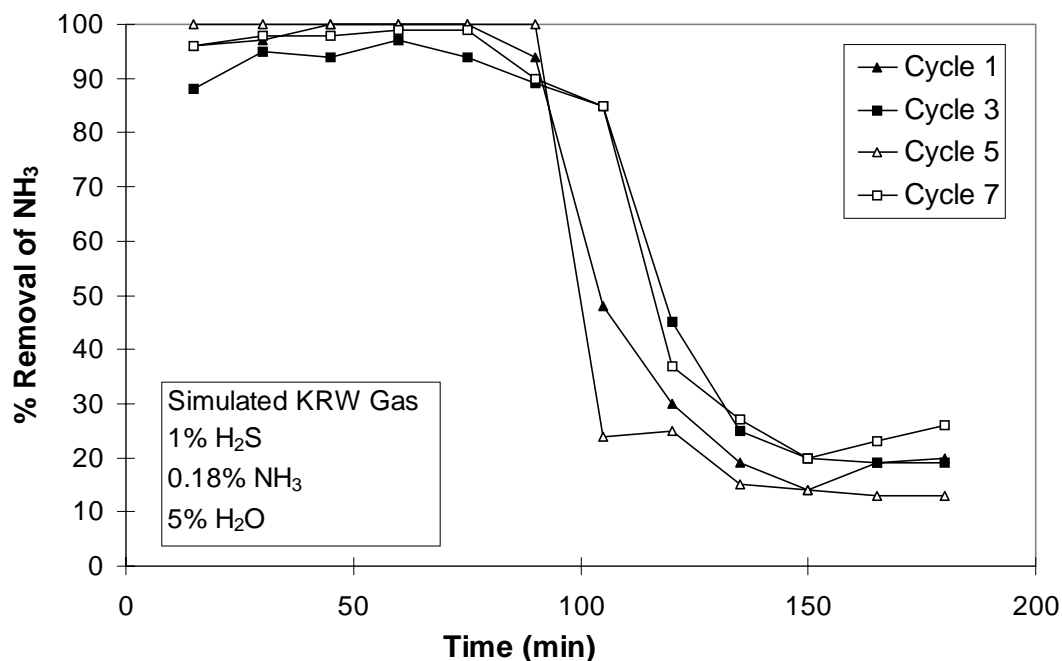


Figure 6. Removal of NH_3 on HART-55 at 550 °C and 10 atm.

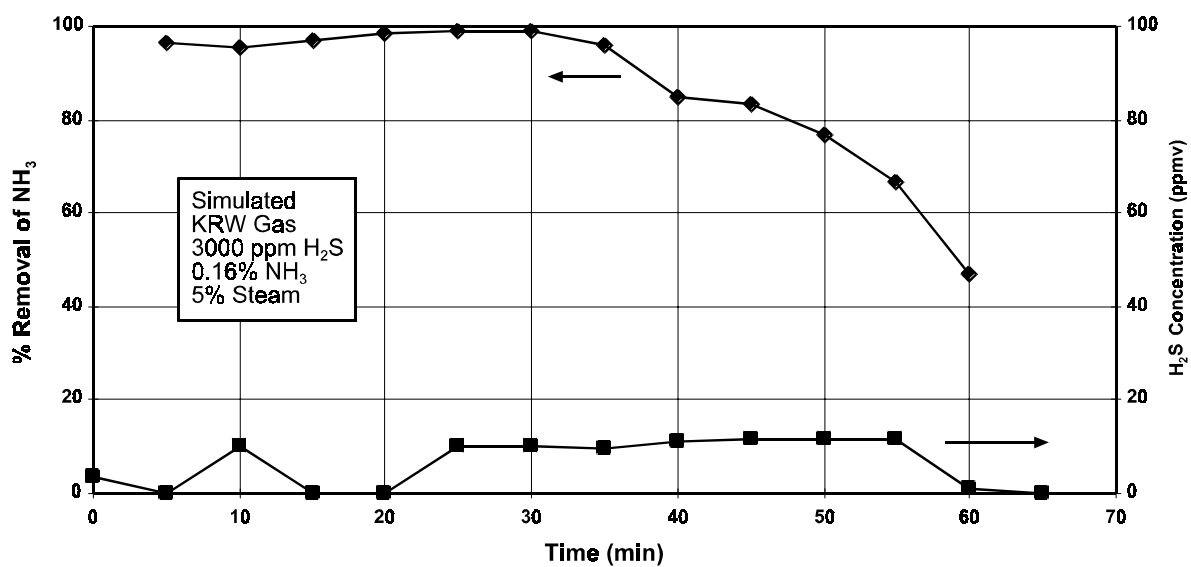


Figure 7. NH₃ and H₂S removal by HART-56 at 20 atm and 550 °C, bench-scale cycles 1 and 2.

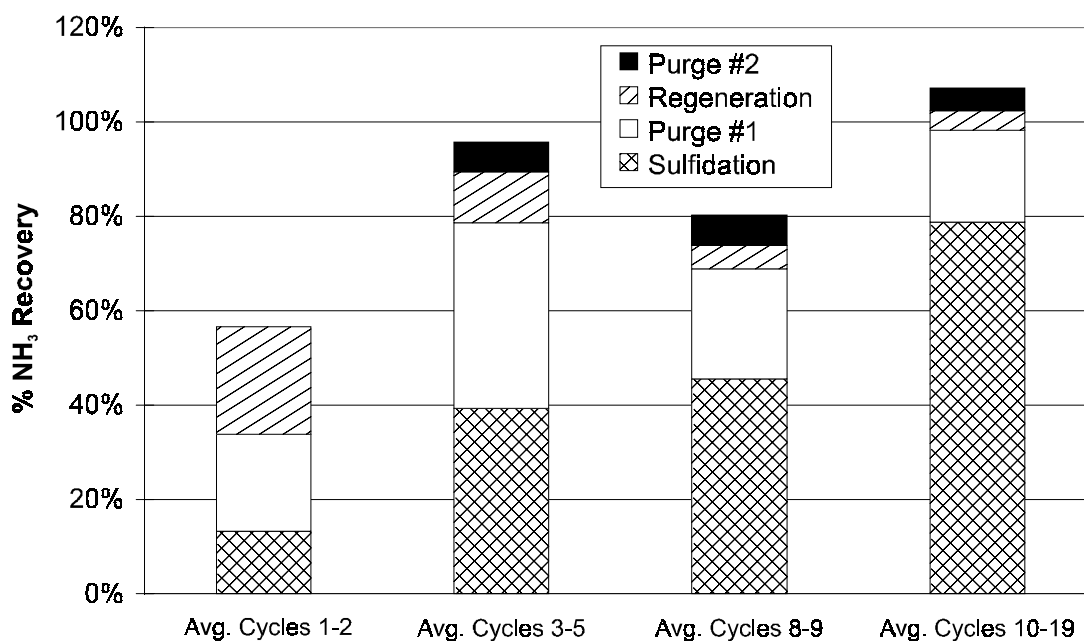


Figure 8. Summary of NH₃ removal and recovery in bench-scale tests.

Application/Benefits

Successful development of a sorbent-catalyst for simultaneous removal of H_2S and NH_3 will result in reducing the overall cost of IGCC systems. HART-49, a lab-scale powder preparation (with high levels of active materials and no binder), showed promising results for simultaneous H_2S and NH_3 removal at 1 atm and 500 to 700 °C. The removal efficiency decreased as temperature decreased but increased significantly as steam concentration in simulated coal gas decreased. Addition of significant level of binder (up to 75 wt%), with corresponding reduction in the amount of active ingredients, resulted in a hard attrition-resistant sorbent-catalyst with better attrition resistance than FCC catalysts. However, its H_2S and NH_3 removal performance deteriorated. The NH_3 removal mechanism on the HART-49-based sorbent-catalysts is complex with reversible adsorption as well as decomposition occurring at higher pressure.

Further work is needed to optimize the sorbent-catalyst preparation to get a balanced material with acceptable attrition resistance, NH_3 removal performance, and cost. With high levels of binder used here, an attrition resistance better than needed was achieved but at the expense of reactivity. The NH_3 removal mechanism needs to be evaluated with fundamental studies, particularly with respect to adsorption behavior on the sorbent-catalyst at higher pressure and the dramatic effect of steam. The attrition-resistant HART-56 sorbent appears to have potential for removing 90 percent NH_3 and reduce H_2S to <20 ppmv, when 5 percent steam is present in the coal gas. However, further development of the material is needed for coal gas with higher steam.

Future Activities

This contract is complete and a final report has been prepared. No further activities are planned.

Acknowledgments

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